

The Reactions of Coal with Transition Metal Halides

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Introduction

Many studies(1) of the X-ray diffraction patterns of coal have yielded the result that increasing coal rank results in increasingly sharp diffraction patterns(2). Furthermore, as the rank limit is approached the very high rank metaanthracites give diffraction with essentially all of the features of a pattern obtained from graphite(3). These results have led to the general acceptance of the model that coalification involves the growth of polynuclear condensed aromatic structures into graphite-like units(1,4). It is of interest to determine if chemical properties of graphite are manifested by coal. In particular, it is well-known that graphite will undergo reactions with a variety of reagents to form intercalation compounds where the graphite layers are separated to accommodate a variety of species between them(5,6). It is therefore of interest to establish if such intercalation compounds can be prepared from coal and, in fact, a recent report very strongly supports that such compounds can be prepared from coal and potassium(7). This paper describes attempts to prepare coal intercalation compounds with the chlorides of iron(III), chromium(III), and copper(II). Analysis of the results is by X-ray powder diffraction. The 002 line in the X-ray powder pattern of graphite is the strongest graphite line and represents the spacing between planar polyaromatic layers of carbon. Formation of intercalation compounds separates these carbon layers and affects this 002 line.

Results and Discussion

Initial experiments(8) were carried out in which anhydrous iron(III)chloride (FeCl_3) was reacted with four different coals. FeCl_3 was chosen for the initial studies because its intercalation compounds with graphite are among the best known and most easily prepared(5,6). The coals selected were the following: PSOC-379, Pennsylvania semi-anthracite (P&M'B'); PSOC-151, New Mexico high volatile bituminous C (Lower Split of Blue); PSOC-240, Washington sub-bituminous B (Big Dirty); and PSOC-247, North Dakota lignite (Noonan). These four coals were treated directly with FeCl_3 after pulverization and air drying at 120° and were also treated with FeCl_3 after a demineralization(9) which involved washing with 10% HCl at 50°C for 18-24 hours followed by air drying at 120° . X-ray diffraction patterns of the untreated and demineralized coals were essentially identical except that enhanced crystallinity of the demineralized samples was evidenced by the shorter diffraction times needed to obtain equivalent diffraction patterns. PSOC-151, PSOC-247, and PSOC-240 showed principally the 002 graphite line whereas PSOC-379 gave this line strongly as well as other lines from crystalline matter.

In each of these six reactions with FeCl_3 approximately 1.0 g of coal and 0.6 g of FeCl_3 were mixed and then heated to 230° for ten minutes. No obvious evidence of reaction was observed and the final

products look similar to the coal starting material. Incorporation of the FeCl_3 into the coal is evidenced by the failure of the reaction products to react readily with water to form the yellow-brown hydrate which the unreacted FeCl_3 forms. The diffraction patterns of the coal- FeCl_3 products of PSOC-151 and PSOC-240 do not include the 002 graphite line which was prevalent in the coal starting material and this line is almost completely eliminated for PSOC-379. More rigorous conditions using 2 g of FeCl_3 per gram of coal and heating for 36 minutes at up to 250° were found to produce products where the 002 graphite line was eliminated for PSOC-379. The products under these more rigorous conditions were observed to be more gray and powdery than the starting coal. The more rigorous conditions required for PSOC-379 could be attributed to more extensive graphite-like structures in the semi-anthracite coal. Examination of the diffraction patterns of the PSOC-247(lignite)- FeCl_3 products gave ambiguous results with removal of the 002 graphite line evident only in the demineralized sample. However, the 002 line in the starting material is relatively weak.

A further observation is the appearance of diffraction lines attributable to $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ in the patterns of some of the reacted samples. This evidence of reduction and hydration of the FeCl_3 was observed for the demineralized samples of PSOC-379, PSOC-151 and PSOC-247, and both dried and demineralized samples of PSOC-240. The nature of the material in the coal which was oxidized was not determined. The H_2O of hydration may have come from moisture still adsorbed on the hydrophilic surface of the coal which may have been rendered more hydrophilic by the demineralization process. Other sources of the H_2O are possible and cannot be overruled.

The demineralized PSOC-379 and PSOC-247 products with FeCl_3 were then washed with 10% HCl at 50° for 18 hours and subsequently dried in air at 120° . The diffraction patterns obtained from the samples after washing were identical to those of the coal samples prior to reaction with FeCl_3 except that a longer time seemed to be needed to obtain the same intensity of diffraction possibly indicating some breakdown of the crystallinity. Thus the reaction with FeCl_3 is largely reversible in these cases. Testing of the wash liquid obtained from these experiments with $\text{K}_3\text{Fe}(\text{CN})_6$ solution gave a strong test for Fe^{++} in corroboration of the X-ray evidence above that $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ is formed in the coal- FeCl_3 reaction.

Comparison experiments were run in which FeCl_3 was reacted with amorphous carbon powder (Acheson Graphite, Grade 38) which can be regarded as microcrystalline graphite. These experiments yielded observations which were parallel to those obtained with coal except that more FeCl_3 and more rigorous conditions were required to eliminate completely the 002 diffraction line of the amorphous carbon. The carbon would be expected to be able to intercalate more FeCl_3 than the much more heterogeneous coal structure. Diffraction lines for $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ were faintly discernible in the diffraction patterns of the carbon- FeCl_3 product and a distinct Fe^{++} test was obtained in the 10% HCl wash liquid. Presumably this can be attributed to adsorbed moisture on the carbon surface and oxidation of some of the carbon.

These experiments were extended to anhydrous chromium(III)-chloride (CrCl_3) and anhydrous copper(II)chloride (CuCl_2). Each of

these salts was reacted with demineralized PSOC-240 and dried PSOC-379 in an approximate ratio of 1.8:1 (g coal: g salt) at 250°. Acidic vapors were evolved in each reaction; the reaction with CuCl_2 resulted in removal of the 002 graphite line but the reaction with CrCl_3 did not. Examination of the coal- CuCl_2 product diffraction patterns did not yield perceptible lines for any material other than CuCl_2 . Washing of the PSOC-379 product with 10% HCl resulted in the return of the diffraction pattern of the starting coal. It was noted that the PSOC-379 had been converted to an extremely fine powder in the course of reaction with CuCl_2 and then washing with 10% HCl. This would seem to be indicative of very extensive penetration of the CuCl_2 into the coal structure.

Further investigations involved the reactions of coal with the corresponding hydrated salts, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. Demineralized and untreated samples of PSOC-379, PSOC-151, and PSOC-240 were reacted with approximately equal weights of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ at 215° for 3 minutes. Each of these mixtures was observed immediately to become liquid and chemical reaction was evidenced by bubbling which occurred for about one minute. At that point the mixtures suddenly solidified and were noticeably more grey in color than the starting pulverized coal. Disappearance of the 002 graphite line was observed in the reactions of the PSOC-379 samples with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and this line was almost completely removed in the PSOC-151 and PSOC-240 reactions. All diffraction patterns of the reacted products showed that $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ had been produced. Washing the products of demineralized PSOC-379 and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ with 10% HCl at 50° brought back the original demineralized coal diffraction pattern although with lines slightly weaker and slightly more diffuse. The liquid remaining from this washing gave a strong test for Fe^{++} again corroborating the formation of $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ in the reaction. Parallel experiments with amorphous carbon resulted in virtual removal of the 002 diffraction line when the ratio of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ to carbon was about 2.5:1 (g:g). No $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ lines were observed in the patterns from the carbon- $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ product and the original carbon diffraction pattern could be returned by washing this product with 10% HCl at 50°.

Reactions of demineralized samples of PSOC-379 and PSOC-151 with $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ both resulted in removal of the 002 graphite lines in the coals. The ratio of coal to salt was about 1.25:1 (g:g) and the reaction conditions were 250° for nine minutes. Dehydration and evolution of acid vapors were evident with both salts; diffraction lines for anhydrous CuCl_2 were evident in the coal- $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ product patterns. No diffraction lines for crystalline salts were evident in the products of the reactions of coal and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. The PSOC-379 diffraction pattern was returned when the products of each of the salts and this coal were treated with 10% HCl at 50°. This washing of the PSOC-379- $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ product again gave back the coal in an extremely finely divided state as was the case in the reaction with anhydrous CuCl_2 (above). Comparison reactions in which $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were reacted with amorphous carbon gave results which were generally parallel to the results of the reactions of these salts with coal except that more salt was needed to effect removal of the 002 line with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and complete removal of this line was not achieved with $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$.

Experimental

Reagents were obtained from standard commercial sources and coal samples were donated by Pennsylvania State University. Powder diffraction patterns were recorded on film using FeK α radiation.

Acknowledgment

The author is grateful to Dr. Alan Davis of the Coal Research Section of the Pennsylvania State University who supplied the coal samples.

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